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TECHNICAL REPORT

Novel Functional Extended Solids at Extreme Conditions

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HDTRA1-09-1-0041

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14. ABSTRACT The main goal of this project has been to demonstrate the existence of novel extended solids at high pressures and temperatures and establish the viability of new functional, high energy density materials such as high-strength, insensitive CN polymers and super-oxidizing extended fluorides. There has been no major change to this original goal, and significant progresses have been made in both discoveries of the proposed functional, high-energy density candidates and developments of enabling technologies for bulk synthesis and characterization of energetic materials.					
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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY → BY → TO GET
TO GET ← BY ← DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter ² (m ²)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm ²)	4.184 000 x E -2	mega joule/m ² (MJ/m ²)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^{\circ}f + 459.67) / 1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter ³ (m ³)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch ² (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m ² (N-s/m ²)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot ²	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch ² (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot ² (moment of inertia)	4.214 011 x E -2	kilogram-meter ² (kg-m ²)
pound-mass/foot ³	1.601 846 x E +1	kilogram-meter ³ (kg/m ³)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0° C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

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1.0 Objectives

The main goal of this project has been to demonstrate the existence of novel extended solids at high pressures and temperatures and establish the viability of new functional, high energy density materials such as high-strength, insensitive CN polymers and super-oxidizing extended fluorides. There has been no major change to this original goal, and significant progresses have been made in both discoveries of the proposed functional, high-energy density candidates and developments of enabling technologies for bulk synthesis and characterization of energetic materials.

A selected set of accomplishments made in this proposal includes:

- Discovered novel 2D and 3D extended solids XeF_2 – candidates for super oxidizer
- Characterized EOS and phase transitions of I_2O_5 and I_2O_6 – oxidizers used in current reactive materials
- Pressure-induced polymerizations in NaCN and TCNE, via 2D C=N polymers, to singly bonded CN polymers – candidates for high strength, insensitive energetic solids.
- Development of transparent large anvil press for synthesis of high-pressure stabilized high energy density solids in bulk (1-5 mg).
- Development of time- and angle-resolved x-ray diffraction capable of probing chemical and structural evolutions across fast energetic reactions.

These accomplishments have resulted in fifteen publications (two in review) in peer-reviewed journals to date and are summarized in this final report, together with other related program accomplishments.

2.0 Status of Effort

This project has been completed on April 4th, 2012 with several major scientific, technological, and educational progresses, including:

- New materials discoveries that can be of considerable value to high strength insensitive energetic materials and super-oxidizing chemical/bio-agents defeat.
- Enabling technology developments for bulk synthesis of high-pressure stabilized extended energetic solids as well as characterization of static and dynamic properties of energetic materials.
- Scientific/technological transitions through (i) fifteen papers in major journals including *Nature Chem*, *Angewandte Chemie Int. Ed.*, and *J. Appl. Phys.*, (ii) thirteen invited presentations including a plenary talk at the APS-SCCM (2009) and invited talks at the GRC on energetic materials (2010), the ACS meeting (2010), the MRS-Fall meeting (2011), the IUCr (2011), and the LANL (2012).
- Significant contributions to education and training of six graduate students and three post-doctoral scientists with hands-on research experiences in cutting-edge technologies and materials of considerable interest to fundamental defense research.

These accomplishments are also significant for understanding fundamental rules in high-pressure chemistry; that is, the pressure-induced electron delocalization into novel extended network structures with more itinerant electrons and larger coordination number and greater density. Novel extended fluorides and CN polymers discovered in the present study, for example, are likely high energy density solids that may be good candidates for the DoD applications in super-oxidizing agents and insensitive energetic materials.

This proposal has contributed to leverage new projects including the DARPA Seedling Grant (W911NF-10-1-0081) on *extended solids-synthesis methods amenable to scale-up and stabilization* and a new DTRA funding on *high-energy-density monolithic organometallic solids*.

3.0 Accomplishments/New Findings

Significant progress has been made in areas of new materials discoveries and enabling technology developments. These are summarized as the following: (A) Functional extended solids -- candidates for super-oxidizing agents, (B) Extended CN polymers -- candidates for insensitive energetic materials, and (C) Technology developments for bulk synthesis and characterization of static and dynamic properties of energetic materials.

A. Functional Extended Solids: Super Oxidizing Candidates

A1. Novel 2D and 3D extended solids and metallization of compressed XeF₂

Metallic fluorine and chlorine are of fundamental significance to condensed matter physics, particularly because they possess behaviors arguably similar to those of hydrogen and lithium. As predicted for hydrogen, the melting maximum, the ground-state liquid metal, and high T_c superconductors are among the surprises that one may encounter in metallic- F or Cl at high pressures and temperatures.

Besides rare-gas solids, fluorine and chlorine are, however, the only two elements that have not been transformed to extended phases. Theoretically, it has been predicted that most low-Z elements do transform into extended solids, either polymeric or metallic, but often at the formidable pressure-temperature conditions above 500 GPa. The high energy density predicted in some of those extended solids is due to high covalent bond energies stored in the 3D network structures and large mass-to-volume ratios. Therefore, an alternative way to produce similar high energy-density extended phases at more practical viable pressures is to form chemical alloys: *i.e.*, extended phases of low-molecular halides (MX_n, where X=F or Cl; M= Li, C, N, O, or Xe), where the low-Z atom (M) creates internal chemical pressure acting on the halide lattice (X).

In this project, we have investigated XeF₂ [1]- one of the most stable noble-gas fluoride compounds, which can be considered as a chemically precompressed, elemental molecular alloy of Xe and F₂ and may provide insight into metallic fluorine below 130 GPa where Xe is known to metallize. In fact, we found that linear molecular XeF₂ is

indeed unstable above 40 to 50 GPa and transforms into novel extended phases. We have made the unexpected discovery of two novel extended solids of rare-gas fluoride XeF_2 at high pressures (see Fig. 1): at around 50 GPa, the transparent linear insulating XeF_2 molecular solid ($I4/mmm$) transforms into a reddish two-dimensional graphite-like, hexagonal layered structure ($Pnmm$) of four-fold coordinated semi-conducting XeF_4 with a Xe-F distance of $1.9 (\pm 1) \text{ \AA}$. Above 70 GPa, it further transforms into a black 3D fluorite-like structure ($Fmmm$) of a first observed eight-fold metallic XeF_8 polyhedron with a Xe-F distance $2.3 (\pm 1) \text{ \AA}$ - well below the metallization pressure of Xe [2,3] and F_2 [4].

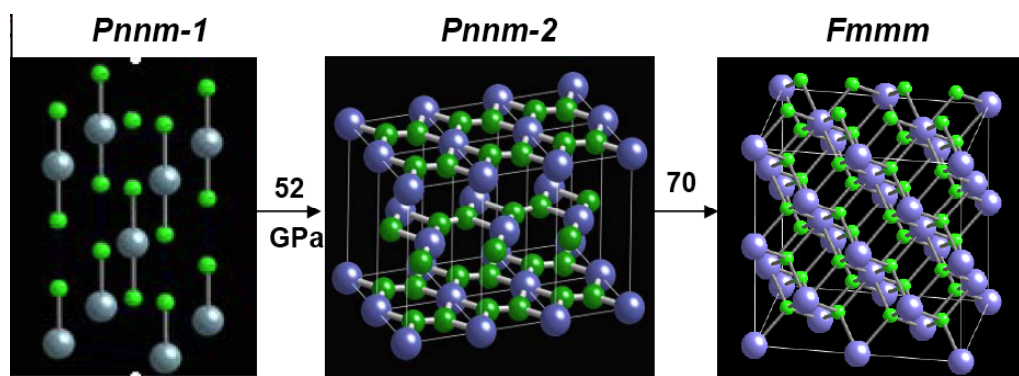


Figure 1. Crystal structures of XeF_2 at high pressures, showing the transition of insulating molecular phase ($Pnm-1$, left) at low pressures to semiconducting graphite-like 2D extended phase ($Pnm-2$, middle) at 52 GPa, and metallic fluorite-like 3D extended phase ($Fmmm$, right) at 70 GPa.

These findings signify fundamental rules in high-pressure chemistry such as π g pressure-induced electron delocalization, from sp^3d hybridized Xe atoms in linear XeF_2 , to sp^3d^2 in 2D XeF_4 , and to p^3d^5 in 3D XeF_8 – a first observed eight-fold coordinated rare-gas solid. It also illustrates how XeF_2 molecules convert nonbonding lone-pair electrons into bonding and, thereby, increase the coordination number, packing efficiency, and density in a tight space, while maintaining the Octet rule. Equally interesting is the bandgap closure at around 70 GPa, well below Xe or F_2 metallization, signifying a basic concept of “molecular alloy”; that is, XeF_2 being a chemically pre-compressed, molecular alloy of Xe and F_2 (as illustrated in Fig. 2).

Extended fluorides can have strong implications for industrial and defense applications. For example, the interatomic interaction of fluorine atoms is very different

from that of C-H-N-O atoms in energetic materials, yet, it is the least known, leading to great uncertainty in the thermochemical description of high explosive detonation. This situation is largely due to experimental difficulties associated with handling highly corrosive and toxic fluorine. An understanding of high-pressure properties (including EOS and melt curves) of fluorine and fluorine-bearing materials is needed to validate the thermochemical models. Extended fluorides are by themselves highly energetic (depolymerizing explosively) and are often used in reactive composite materials (e.g., Al-Teflon). Furthermore, because of the large ionization potential of fluorine (3.06 eV in comparison with OH^o 2.84 eV, O 2.42 eV, O₃ 2.07 eV, and H₂O₂ 1.77eV), the fluorine-containing groups are super oxidizers and exhibit strong chemical and biological effects. Thus, extended fluorides can be used to neutralize (or mineralize) bio/chemical warfare agents, as well as to disinfect contaminated environments.

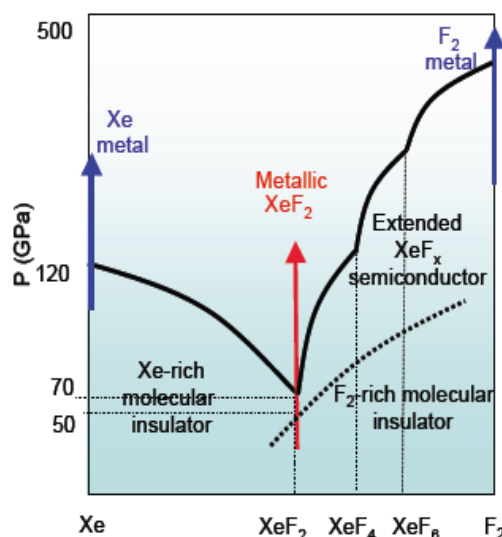


Figure 2 A schematic to illustrate XeF₂ as a novel molecular alloy of elemental Xe and F₂. This concept stems from the fact that XeF₂ metallizes at 70 GPa, a substantially lower pressure than those of F₂ and Xe. The low metallization pressure 70 GPa of extended XeF₂ then reflects its eutectic and/or precompressed state.

A2. EOS and phase/chemical transformations of oxyhalides: I₂O₅

We have also investigated the structure and phase transitions in recently synthesized high-density oxy halides, both I₂O₅ and I₂O₆ – likely a high energy containing super oxidizer [5,6]. The sample was synthesized by the USC group (Profs. Priya Vashishta and Karl Cristie). We summarize the results of I₂O₅ here, while the work on I₂O₆ is still in progress.

We have measured, for the first time, Raman and powder x-ray diffraction of I_2O_5 under pressure up to 32 GPa. The results indicate that there are three phases transitions at room temperature: two solid-solid transitions at ~ 5 and ~ 15 GPa and irreversible polymerization at ~ 23 GPa (see Fig. 3). Monoclinic structure, space group $P2_1/c$ [7] remains unchanged up to 21 GPa, which suggests I_2O_5 undergoes isostructural phase transition under pressure. Complex Raman features, at phase II and III, were due to the transformation of monomeric I_2O_5 to polymeric structure associated with increasing the coordination number of iodine from three to five. Simultaneously, one dimensional chain structure transforms via a two dimensional stacking layer to a three-dimensional network structure. All oxygen atoms participate on the I-O bonds with the bond distance within $\sim 1.6\text{\AA}$ to $\sim 1.9\text{\AA}$, which is much shorter than the I-O bonds in the pseudo-polymeric I_2O_5 cluster produced by the van der Waals interaction. We consider an anisotropic van der Waals interaction to be a primary driving force of the peculiar monomeric I_2O_5 structure, which causes the observed distortion in local structure of low-pressure phases [8]. According to the characteristic I-O distance and associated I-O-I bond angle, we suggest two types of oxygen-iodine bonds to exist. The bulk modulus of solid I_2O_5 , $B_0 = 19.7$ GPa with $B_0' = 9.9$ GPa, was obtained by using third order Birch-Murnaghan equation of state (Fig. 4).

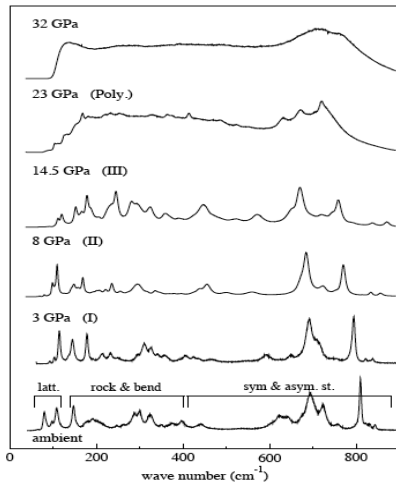


Figure 3. Raman spectra of I_2O_5 from ambient pressure up to 32 GPa at room temperature, showing the evolution of Raman spectra with pressure and the corresponding phase transitions.

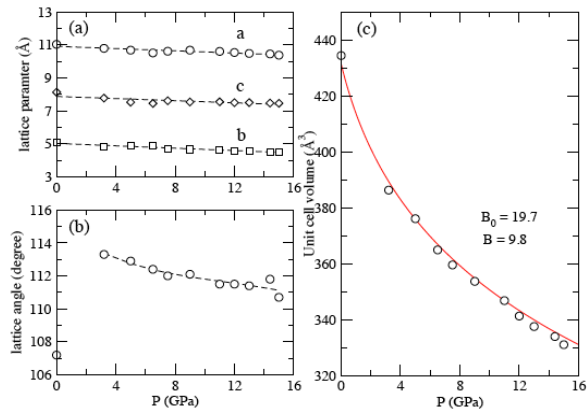


Figure 4. The evolutions of lattice parameters (a), angle (b) and specific volume (c) of I_2O_5 , as a function of pressure. The data are fitted to a 3rd order Birch-Murnaghan equation of state (red line) with $B_0 = 19.7$ GPa and $B' = 9.8$. The blue square box represents an ambient pressure unit cell volume.

B. Extended CN Polymer: Insensitive Energetic Materials Candidates

B1. Physical and chemical transitions of sodium cyanide at high pressures

Low Z extended solid is a new class of high energy-density material. The existence of such materials has recently been demonstrated in polymeric N_2 and CO . However, because they are so energetic (containing energy up to several *times* that of conventional explosives), these materials are highly unstable at ambient conditions and are usable only with a substantial level of chemical passivation and/or desensitization. On the other hand, similarly high energy density but chemically stable polymers can be made of strong carbon-nitrogen covalent bonds. CN compounds are known to exist in a wide array of chemical configurations that can be converted into *1D*-chain, *2D*-ladder, and *3D*-network structures. Such chemical variety enables one to produce CN-polymers at more practical PT conditions, as well as to control the meta/stabilities, sensitivities, and energetics and, thereby, obtain insensitive, high energy-density CN polymers.

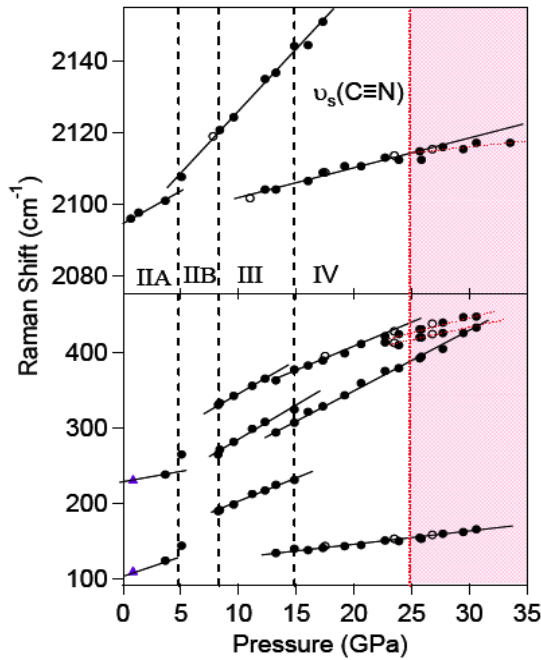


Figure 5. The pressure dependence of vibrational Raman modes: the external lattice modes in the bottom panel and the internal $C\equiv N$ stretching mode in the upper panel. The solid (or open) symbols are the data obtained during pressure uploading (or downloading). The dashed lines indicate the transition pressures and the dotted line indicates the lowest pressure where the $C=N$ stretching mode is noticeable. The reddish area signifies the region of chemical reaction.

We have investigated the pressure-induced physical and chemical changes in a few alkali metal nitrides including NaCN and KCN, using micro-Raman, angle-resolved x-ray diffraction, and laser-heated diamond anvil cells. We found three phase transitions in NaCN to 50 GPa as shown in Fig. 5 [9]: NaCN-IIA (orthorhombic, $Immm$), to NaCN-IIB (orthorhombic, $Pmmn$) at 4 GPa, to NaCN-III (monoclinic, Cm) at 8 GPa, and to NaCN-

IV (tetragonal, $P4mm$) at 15 GPa, which is stable to 25 GPa. At higher pressures, NaCN-IV undergoes an irreversible chemical change, which occurs over a large pressure range between 25 and 34 GPa. The new material exhibits a broad yet strong Raman band at around 1600 cm^{-1} , indicating the formation of C=N bonds in a similar configuration of carbon graphite.

These results are significant in finding three phase transitions: from phase IIA ($Immm$) to IIB ($Pmmn$) at 4 GPa, to III (Cm) at 8 GPa, and to IV ($P4mm$) at 15 GPa, as well as a chemical transformation of phase IV at 25 GPa. This result clarifies the phase diagram of NaCN in the region between 8 and 15 GPa, which follows the general structural trend of alkali cyanides from cubic to orthorhombic ($Immm$ and $Pmmn$), and to monoclinic (Cm). However, the tetragonal phase IV ($P4mm$) above 15 GPa has not been observed in other alkali cyanides, presumably due to its high stability pressure. The layer structure of phase IV is consistent with its chemical reaction yielding a layered CN polymer.

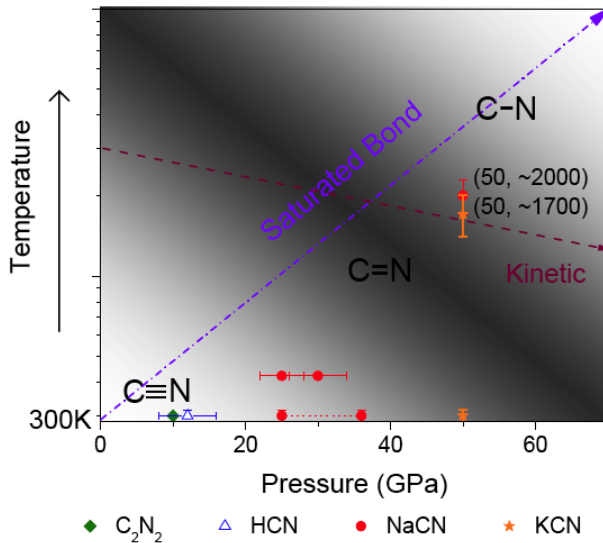


Figure 6. A chemical diagram to illustrate the pressure-induced chemical transitions of RCN ($R=CN, H, Na, K$) compounds into extended 2D and 3D-CN polymers. It illustrates the stepwise polymerization from $C\equiv N$ to $C=N$ to $C-N$. The $C-N$ polymer is likely a hard material that may have a potential for development of insensitive high energy density solids.

Continuing the structural phase transition studies, we have also examined the chemical reactions of NaCN and KCN at higher pressures and temperatures, by using laser-heated diamond anvil cell techniques. The result shows that these molecules undergo a stepwise polymerization: first to graphite-like C=N polymers at around 30 GPa for NaCN and 50 GPa for KCN, at the ambient temperature, then to transparent C-N

polymer at high temperatures around 1500-2000 K at these pressures, as illustrated in **Fig. 6**.

The pressure-induced electron delocalization or hybridization is responsible for the observed polymerizations; yet, the detailed mechanism has not been understood, nor has the crystal structure of the C-N polymers. We are currently characterizing the structure of the C-N polymers, in order to examine if it has any structural relationship with the earlier proposed superhard CN polymers such as β -C₃N₄ [10] or cubic-CN [11] polymers. Furthermore, the CN-polymers synthesized in the present study are likely in high energy states. Under the right conditions, they may exothermically depolymerize to hot carbon particles and nitrogen gases. The energy liberated from strong covalent bonds in this process can exceed that of conventional explosives. While these CN polymers are recoverable at the ambient conditions, the transition pressures are relatively high (30-50 GPa) for synthesis of a bulk quantity (1 mg) that would require the investigation of its energetics. Therefore, we are planning to explore an alternative way using HCN and C₂N₂.

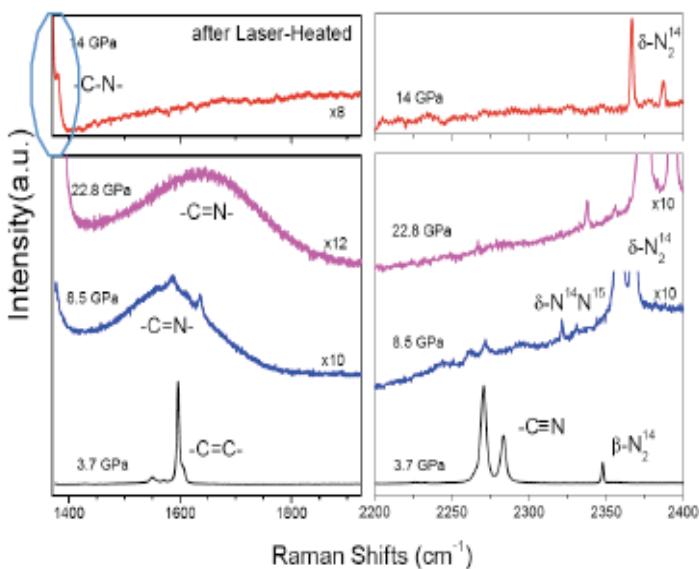


Figure 7. Raman spectra of TCNE under high pressures showing the pressure induced polymerization from C \equiv N to C=N at 12 GPa and upon laser heating to C-N above 20 GPa. The top spectra at 14 GPa was initially produced at 20 GPa by laser-heating C=N products.

B2. Pressure-induced polymerization of TCNE (C₆N₄)

Another system that we have investigated recently was tetracyanonitrile ethylene (TCNE, C₆N₄) to produce a CN polymer. Unlike RCN (R=alkali metals), this material is purely consisted of carbon and nitrogen and results in a substantially simpler transformation and, more importantly, at substantially lower pressures as shown in **Fig. 7**. The spectral results

show that the $C\equiv N$ groups in TCNE converts to the $C=N$ in 2D graphite-like, black CN-polymer and then to the $C-N$ in 3D transparent CN polymer above 20 GPa. These results again confirm the stepwise transformation observed in other RCN. The x-ray data was also obtained to 40 GPa, and the analysis is currently underway [12].

Interestingly, the laser-heated poly-CN exhibits the laser-induced fluorescence centered at around 670 nm (**Fig. 8** left) analogous to nitrogen-doped nano-diamonds (the inset). The nature of fluorescence is known to arising from the excitonic states of nitrogen-lattice vacancy defects: $(N-V)^*$ at 580 nm and $(N-V)^-$ at 640 nm [14]. These sharp features are not apparent in the poly-CN (except a little remnant of the peak at ~640 nm), which is probably due to a substantially greater amount of nitrogen content and thereby broadening of the excitonic state (or band).

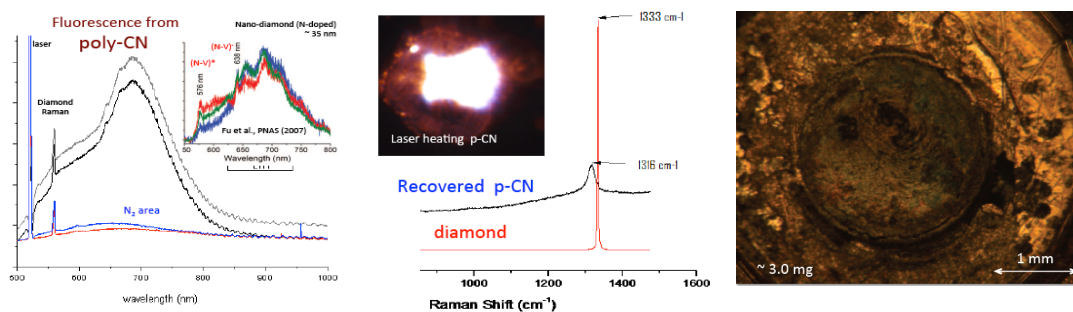


Figure 8. (Left) A laser-induced fluorescence of laser heated poly CN at 20 GPa, showing a spectral similarity with that of nano-diamond with nitrogen impurities in the inset. (Center) Raman characteristics of recovered poly-CN in comparison with that of diamond. (Right) Poly-CN sample synthesized in bulk quantity (~3 mg) by compressing TCNE to 13 GPa using our TLAP.

The recovered sample after laser heating TCNE shows the Raman characteristic similar to that of nano-diamonds (**Fig. 8** middle) [15]. The Raman peak of $\nu_s(C-N)$ is broad, similar to 30-40 nm nano-diamonds, yet the peak position is substantially down-shifted by $\sim 20 \text{ cm}^{-1}$ from pure single crystal diamond and also $\sim 10 \text{ cm}^{-1}$ from 30 nm-size nano-diamond. This signifies the presence of nitrogen in this polymer.

Note that both poly-CN and nano-diamonds are likely candidates for super-hard high energy density solids. Therefore, it is of interest to the present project. Hence, we

have further synthesized the poly-CN for further characterization (**Fig. 8** right). The sample was recovered after compressing TCNE to 13 GPa, which weighs about 2.95 mg. We are currently working on characterizing the sample – especially of its energy content and hardness.

B3. Novel nitrogen-rich chemical alloys: $N_2(D_2)_{12}$

Extended forms of simple low-Z materials, such as the recently discovered *cubic gauche* form of polymeric nitrogen (*cg-N*), are of fundamental importance in developing condensed matter theory and novel materials with advanced mechanical, optical, and energetic properties. The energy content of this material (33 KJ/g) is expected to be at least three times of that of HMX (10 KJ/g) [16]. These materials are, however, typically stabilized at formidable pressure-temperature conditions, thus imposing tremendous technical challenges to be useful.

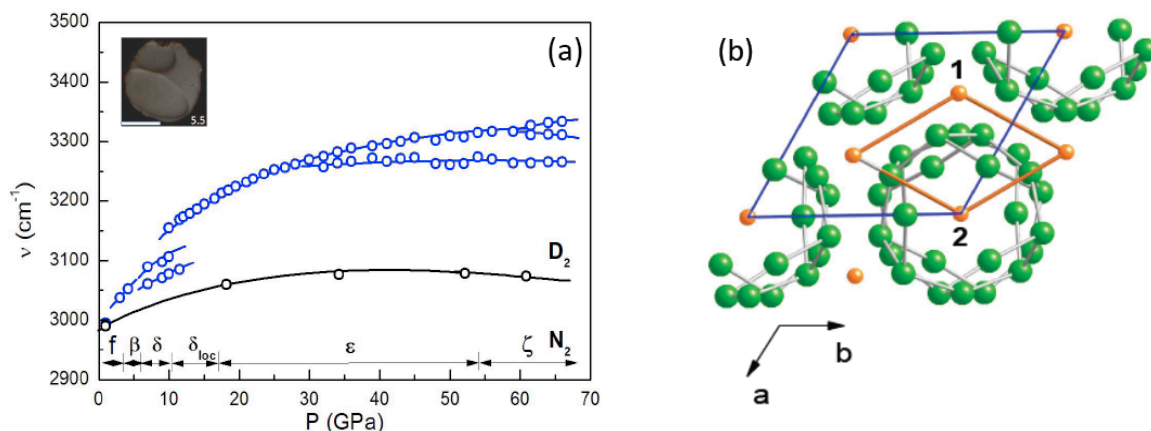


Figure 9. (a) The pressure dependence of D_2 vibron in the 9:1 N_2 and D_2 mixture and, in the inset, the microphotograph of the sample at the onset of freezing at 5.5 GPa, showing two large pieces of plastic solids and surrounding liquid. The phase transition pressures of pure N_2 (dotted-lines at the bottom) and the pressure dependence of pure D_2 vibron [15] (open symbols) are also shown for comparison. (b) The proposed crystal structure of hexagonal $(N_2)_{12}D_2$ with the molecular positions of 24 N_2 (green) and 2 D_2 (orange) on a projection of the *ab*-plane.

Following the same objective to synthesize nitrogen-rich extended solid, in this project we have employed an alternative synthetic route utilizing chemical impurities such as hydrogen. This concept stems from the concept of novel chemical alloys that we have developed and described for XeF₂ [17]. That is, to create a large chemical internal

pressure in the nitrogen lattice by introducing small materials like hydrogen and thereby reduce the transition pressure to cg-N or similar extended phase nitrogen-rich solid.

In this investigation, we found the spectral and structural evidences for formations of a homogeneous cubic δ -N₂-like, non-crystalline plastic solid and an incommensurate hexagonal ($P6_322$) inclusion compound (N₂)₁₂D₂, formed by compressing a nitrogen-rich mixture to 5.5 and 10 GPa, respectively (**Fig. 9**) [18]. The 9:1 N₂-D₂ mixture freezes at 5.5 GPa into a homogeneous plastic solid (**Fig. 9a** inset) – a substantially higher pressure than that at which pure N₂ freezes into β -phase but at the onset of pure-D₂ solidification. Above 10 GPa, the plastic mixture transforms into a new phase, which exhibits a singlet of D₂ vibron at substantially higher wave numbers, and a doublet of N₂ vibron with substantially reduced relative intensity of the ν_2 . Based on the Raman characteristics and the x-ray diffraction data, we have proposed the crystal structure of this new phase to be in hexagonal $P6_322$ (as shown in **Fig. 6b**), which contains 24 N₂ molecules and two D₂ molecules at the interstitials. Based on the selected D₂ positions, either fully filled or partially filled, a hexagonal sub-lattice (orange-colored line in **Fig. 9b**) was formed with a long-range order periodicity, which means the N₂-D₂ compound is a typical incommensurate system.

This new hexagonal phase is stable at least to ~35 GPa, above which the singlet of D₂ vibron, again, splits into two, signifying yet another phase transition at 35 GPa. Based on the Raman characteristics, we find that these transitions in the mixture are well in one-on-one correspondence to those in pure N₂, indicating that above 35 GPa is likely the ζ -N₂ like phase – the phase polymerizes to cg-N above 110 GPa and 2000 K in pure N₂ [19]. A strong repulsive is evident from a blue shift, discontinuous shifts, and the absence of turnover of the D₂ vibron to 70 GPa – all in sharp contrast to both pure D₂ and other inclusion compounds. This repulsive interaction is responsible for the observed incommensurate structure and large internal pressure mentioned above.

C. Technology Developments

C1. Transparent large anvil press (TLAP)

One of the objectives of this project is to demonstrate the scale up synthesis and novel properties of a few selected systems. In order to accomplish this objective we have begun to develop a high-pressure cell capable of synthesizing a mg-quantity sample. The mg-quantity sample is important in order to demonstrate its novel properties needed for practical applications such as energy content, hardness, impulse characteristics, structures of disordered systems, etc. Furthermore, it is a key step of scaling up to even larger scale in grams, pertaining the same sets of engineering developments.

This developmental effort has been leveraged by the DARPA. For the design, we have considered the following key issues: (i) permitting a large load (10-50 ton) to accomplish the required pressure and sample size, (ii) allowing efficient and prompt loading of samples under cryogenic conditions, and (iii) providing optical access to the sample chamber for *in-situ* laser heating, Raman and other spectroscopy measurements. In order to implement these key features in design, we have developed a transparent large anvil press (TLAP), which consists of a transparent large anvil cell (TLAC) and a 50-ton large volume press (LVP) of a modified Paris-Edinburgh cell (PEC), as shown in **Fig. 10**.

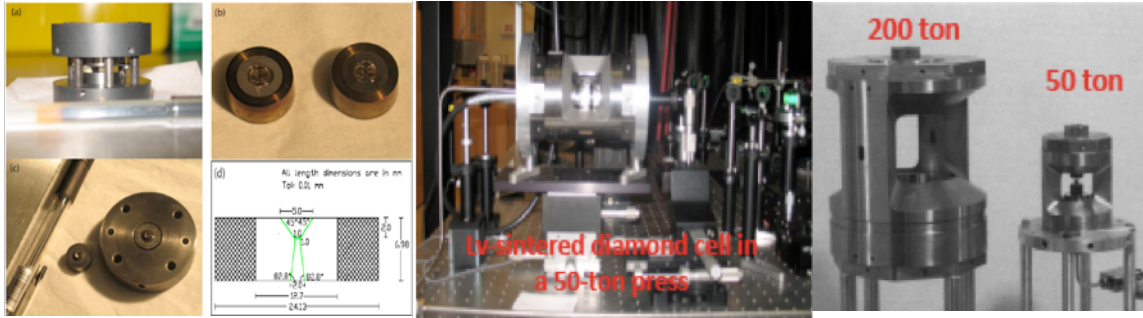


Figure 10. (Left) A custom-designed transparent large anvil cell (TLAC) utilizing two opposed diamond anvils supported in WC or sintered diamond seats in a Bridgman configuration. (Center) Transparent large anvil press (TLAP) which consists of a TLAC and a 50-ton press of Paris-Edinburgh type, which is able to transmit a required large force on to a large diamond flat and to perform *in-situ* Raman spectroscopy, laser-heating, and optical/visual observation of a bulk quantity sample, (Right) an engineering concept of scale-up using a 200 ton press.

With TLAP, we were able to load liquid N₂ and liquid CO₂ samples and by performing Raman spectroscopy measurements on them [20]. Additionally, it is capable of *in-situ* laser heating on samples at pressures greater than 15 GPa. Both the

experimental arrangement for optical measurements and the mechanical design of the complete TLAP assembly are very general and can be adapted to a wide variety of different LVP configurations for further scaling up.

C2. Time- and Angle-Resolved Synchrotron X-ray Diffraction

Understanding the dynamic response of solid under extreme conditions of pressure, temperature and strain rate is a fundamental scientific quest and a basic research need in materials science. Specifically, obtaining the atomistic/molecular level description of structural and chemical changes of solid under rapid heating and/or compression over a large temporal, spatial and energy range is critical to understanding material stability or metastability, transition mechanism, crystal order or disorder, and novel physical and chemical properties of solids. It is also in significance to the present project, in ways to investigating dynamic responses of new energetic materials, especially mechanisms of energetic processes and energetic performance.

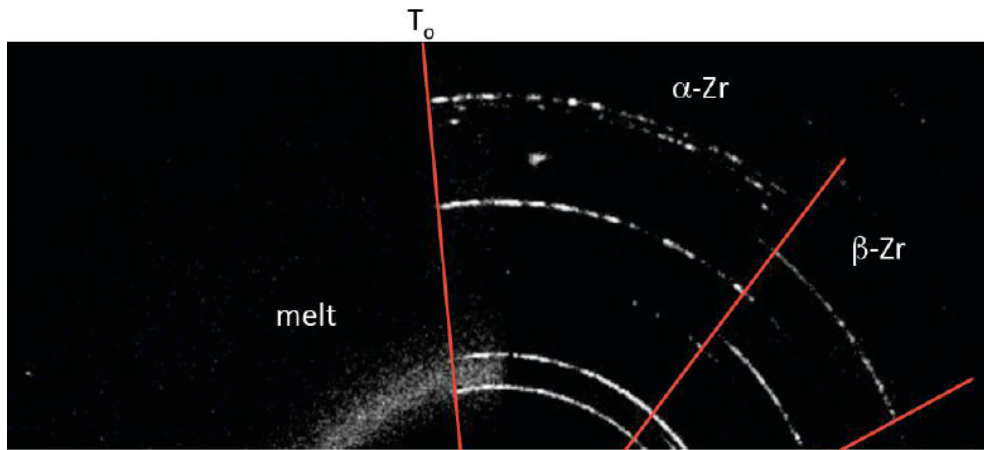


Figure 11. Time- and angle-resolved x-ray diffraction of pulse-heated Zr, showing the early time structural phase transition and melting, followed by the late time highly exothermic combustion of the melt (not shown). This 2D diffraction pattern was recorded for $\sim 30 \mu\text{m}$ x-ray exposure over $\sim 3 \text{ ms}$. Time runs clockwise from T_0 - cocentric to the Debye-Scherrer's diffraction rings.

The high brightness of third-generation synchrotron x-rays has revolutionized the field of high-pressure material science and geoscience in recent years. High-pressure synchrotron research activities to date have, however, concentrated largely on probing static properties of materials that are stable near minimum energy configurations and

governed by thermodynamic constraints. Only a few studies have acquired dynamic properties of materials such as metastable structures, chemical mechanisms, transition dynamics, and mechanical deformation, much of which require the time-resolved structural information of solid that undergoes rapid phase or chemical changes. In this regard, developing time-resolved x-ray diffraction capabilities is significant for high-pressure sciences and synchrotron technology developments. It is also timely with the proposed development of dynamic compression beamlines at the APS and other similar efforts at the NSLS-II and LCLS.

The machine characteristics of third-generation synchrotron are ideally suitable for probing dynamic single-event phenomena such as shock-induced phase changes and highly exothermic metal combustions. As the first step, we have recently demonstrated a novel time-resolved x-ray diffraction capability probing structural and chemical evolutions of metallic solids that undergo rapid phase and chemical changes [21,22]. The experiments were performed using monochromatic synchrotron x-rays at the 16IDD beamline at HPCAT/APS and a 2D PILATUS x-ray detector coupled with a fast running chopper. Multiple frames of 2D powder x-ray diffraction images (Fig. 11) were recorded with a time resolution of 10-50 μ s over a long time period of 3-several 100 ms, probing real-time structural changes. The present method is applicable to a wide range of dynamic experiments to study both single event phenomena of solid under thermal, electric or mechanical impact conditions and non-single event changes using dynamic-DAC and high frequency pulse lasers.

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22. H. Wei and C.S. Yoo, *Kinetics of small single particle combustion of zirconium alloy*, *J. Appl. Phys.* 111, 023506 (2012).

702 Personnel Supported

The present project has been supporting the efforts of the following personnel:

- Principle investigator Choong-Shik Yoo, who has directed the project progress
- Two postdoctoral researchers, Minseob Kim and Jing-Yin Chen, who have performed the major parts of experiments on x-ray diffraction and Raman spectroscopy, respectively;
- Two graduate students, Dane Tomasino and Mihindra Dunuwille, who are participating in this and other related projects.

8.0 Publications

Fifteen papers, two in review and the rest in print, have resulted in publications in support of this tgr qtv

1. M. Kim and C. S. Yoo, *EOS and phase transitions in I_2O_5 under pressures: Raman and X-ray Diffraction Studies*, **J. Chem. Phys.**, submitted (2012).
2. H. Wei and C. S. Yoo, *Dynamic responses of reactive metallic structures under thermal and mechanical loadings*, **J. Mater. Res.**, submitted (2012).
3. H. Wei and C. S. Yoo, *Dynamic structural and chemical responses of energetic solids*, an invited paper to 2011 MRS Fall Meeting, in print.
4. A. Sengupta, Y-J. Ryu, and C. S. Yoo, *Transparent large anvil press for in-situ Raman and laser heating*, **J. Phys. C**, in print (2012).
5. H. Wei and C.S. Yoo, *Kinetics of small single particle combustion of zirconium alloy*, **J. Appl. Phys.** 111, 023506 (2012).
6. C. S. Yoo, H. Wei, J. Y. Chen, G. Shen, P. Chow, and Y. Xiao, *Time- and angle-resolved x-ray diffraction to probe structural and chemical evolution during Al-Ni intermetallic reactions*, **Rev. Sci. Instrum.** 82, 113901 (2011).
7. Choong-Shik Yoo, Amartya Sengupta, and Minseob Kim, *Carbon dioxide carbonates in the Earth mantle: Implications to the Deep Carbon Cycle*, **Angew. Chem. Int. Ed.** 50, 11219 (2011).
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9. Choong-Shik Yoo, Amartya Sengupta, and Minseob Kim, *Phase diagram of carbon dioxide: Update and challenges*, **High Pressure Research** 31, 68-74 (2011).
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15. Jing-Yin Chen and Choong-Shik Yoo, *Physical and Chemical Transformations of Sodium Cyanide at High Pressures*, **J. Chem. Phys.** 131, 144507 (2009).

900 Interactions/Transitions

a. *Participation/presentations at meetings, conferences, seminars, etc.*

The PI and his group members have presented the major results accomplished in this proposal at national/international workshops, conferences, and seminars on the related subjects. Here, we list only invited/plenary talks presented by the PI:

1. *Chemical Stability of Energetic Materials at High Pressures*, an invited talk to 2012-Chemistry under Extreme Conditions, an invited talk to Los Alamos National Laboratory, Jan. 18-20th, 2012, Santa Fe, New Mexico.
2. *Chemistry at Extreme Conditions: Recent Data and Future Perspectives*, an invited talk to 2012-Chemistry under Extreme Conditions, Los Alamos National Laboratory, Jan. 18-20th, 2012, Santa Fe, New Mexico.
3. *Dynamic Structural and Chemical Responses of Energetic Solids*, an invited talk to 2011 Fall-MRS Meeting, Nov. 29 - Dec. 2, 2011, Boston, Massachusetts.

4. *Time and Angle-resolved X-ray Diffraction (TARXD): Probing Structural and Chemical Evolutions*, an invited talk to the AIRAPT-23, Sept. 25-30, 2011, Mumbai, India.
5. *High Pressure Research at WSU: Monolithic High Energy Density Materials*, a Colloquium at Materials Science and Engineering Program, WSU, Sep. 16, 2011
6. *Time and Angle-resolved X-ray Diffraction (TARXD): Probing Structural and Chemical Evolutions*, an invited talk to the XDL Workshop 4 on High Pressure Science on the Edge of Feasibility, Cornell University, June 23-24, 2011.
7. *High Pressure Research at WSU: Chemistry Beyond Static Properties*, an seminar at Physics Department, University of Nevada, Las Vegas, March 29, 2011.
8. *Novel Solids at Extreme Conditions*, an invited talk to PacifiChem 2010, Dec. 15-19, 2010, Honolulu, Hawaii
9. *Synthesis of Extended Solids at Extreme Conditions*, an invited talk to IUCr-HP 2010, Sept. 19-23, 2010, Gatlinburg, TN.
10. *High Pressure Chemistry: Chemistry Views of Pressure-induced Phase Transformations*, a lecture in the CDAC Summer School, Sept. 15-18, 2010, HPCAT/APS, Argonne, IL.
11. *Novel Extended Phases of XeF_2 and CO_2 under Extreme Conditions*, an invited talk at the Kick-off Conference on Pressure Effects on Materials, Aug. 22-27, 2010, ICMR, UC Santa Barbara, CA.
12. *Phase Diagram of Carbon Dioxide: Update and Challenges*, an invited talk presented at the 48th European High Pressure Research Group Conference, Uppsala, Sweden, July 25-29, 2010.
13. *Monolithic Extended Solids*, an invited lecture at 2010 Gordon Conference in High Explosives, Tilton School, Tilton, NH, June 13 – 18, 2010

b. Programmatic leverage

The present project has been leveraged by the DARPA-Seedling project, especially in construction of the transparent large anvil press (TLAP).

c. Organizing the scientific workshop related to the project matter.

Organized a DTRA-supported Symposium Y on Advances in Energetic Materials Research at the 2011 MRS-Fall meeting, Nov 28 – Dec 2, 2011, Boston, MA. This workshop was attended by over 100 attendees with the total of 80 invited/contributing papers presented at this three-day (Nov. 28-30) focused session. Among those presented, twenty-eight papers were published on line (Please see the articles in: <http://journals.cambridge.org/action/displayIssue?jid=OPL&volumeId=1405&iid=8468970> and four papers have been recommended for publication to J. Mater. Res.. In the meeting, five graduate students were awarded for best presentations, including Gregory Fritz at Johns Hopkins University; Carrisa Goldstein at North Carolina State University; David Kolesky at University of Illinois, Urbana-Champaign; Nicholas Piekiet at University of Maryland; and Katie Browning at U. of Tennessee. Each were awarded a cash prize of \$400.00 that can be reimbursed from our symposium's fund provided by support of the DTRA, LLNL, and MRS.

d. Transitions:

The scientific accomplishments in this project have made transitions to a broader scientific community in several ways: (i) publications in peer-reviewed journals and scientific presentation in workshops (see, the section vi and vii-a), (ii) mutual programmatic interactions with other related DoD projects and complexes (see, the section vii-b), (iii) organizing a large scientific format on the subject matter related to the project (see, the section vii-c), (iv) providing the data generated in this project is significant for explosives modeling and is expected to be incorporated into the explosive database such as Cheetah, etc., and (v) training graduate students and postdoctoral researchers on the DoD defense research needs and ultimately providing future workforce in the DoD complexes.

:.0 New discoveries, inventions, or patent disclosures

No patent or record of invention has been filed, but technical reports published in scientific journals as listed in Sectionu *vi* and *vii*, regarding:

- Discovered novel 2D and 3D extended solids XeF_2 – candidates for superoxidizer.
- Discovered extended CN polymers from NaCN and TCNE – candidates for insensitive energetic materials.
- Developed transparent large anvil press (TLAP) for high-pressure synthesis of bulk samples (1-5 mg).
- Developed time-resolved synchrotron x-ray diffraction capable of probing chemical and structural evolution during single event combustion-like reactions.

;00 Honors/Awards

Dane Tomasino, a Ph.D. graduate student in the PI group, has received the *2012 Harold Dodgen Award* on his Ph.D. research progress on *TCNE and high density fluids*, performed in support of this project.

3200 Quad Chart



Novel Functional Extended Solids at Extreme Conditions Choong-Shik Yoo, WSU, HDTRA1-09-1-0041

Objectives:

- Demonstrate the existence and viability of monolithic high-energy density (HED) extended solids:
 - Insensitive high-strength polymeric CN
 - Superoxydizing extended fluorides

Challenges:

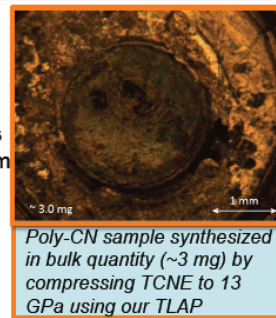
- Understand novel states of matter at extreme conditions, and solid state chemistry in general
- Develop a new concept of functional energy materials: superhard, insensitive HE, superoxydizers
- Understand pressure-induced electron delocalization

Major Accomplishments:

- The project is well on track toward the goal to demonstrate the proposed proof-of-the-concepts:
- Discovered several systems of novel functional HED candidates: (i) supeoxidizer extended XeF_2 and I_2O_6 , (ii) high strength CN polymers, and (iii) nano-diamonds and diamond-like carbons
- Technology developments: (i) completion of constructing transparent large volume press and synthesis of bulk CN polymer (3 mg) and (ii) time-resolved diagnostics for investigation of dynamic responses of HED solids.

Key Concepts:

- Storing large mechanical energy ($P\Delta V$) into strong chemical bond energy of monolithic extended solids – the most condensed form of energy storage outside the nuclear energy
- Building functional HED solids based on novel properties of low Z elements



Status of the Efforts: Completed

Personnel Supported:

6 GS (~50%), 3 PD (~50%) and PI(~10%)

Publication and Meeting:

- 15 manuscripts published (2 in review).
- 12 invited talks at ACS, GRC_HE, U of I, UNLV, Cornell
- 1 plenary talk at the APS-SCCM

Funding Profile:

\$ 520,880 K out of \$521,026 K to June 1, 2012.

PI: Choong-Shik Yoo; csyoo@wsu.edu; (509) 335 - 2712

13.0 Markings

This is the final report of the DTRA project, HDTRA1-09-1-0041.

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